



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08F 10/00, 4/64		(11) International Publication Number: WO 99/14250 (43) International Publication Date: 25 March 1999 (25.03.99)
<p>(21) International Application Number: PCT/CA98/00839 (22) International Filing Date: 3 September 1998 (03.09.98)</p> <p>(30) Priority Data: 2,215,444 15 September 1997 (15.09.97) CA</p> <p>(71) Applicant (<i>for all designated States except US</i>): NOVA CHEMICALS (INTERNATIONAL) S.A. [CH/CH]; Route de la Glane 107, P.O. Box 76, CH-1752 Villars-sur-Glane 1 (CH).</p> <p>(72) Inventors; and (75) Inventors/Applicants (<i>for US only</i>): MCMEEKING, John [GB/CA]; 639 - 14 Avenue S.W. #1108, Calgary, Alberta T2R 1H9 (CA). GAO, Xiaoliang [CA/CA]; 6 Varmoor Place N.W., Calgary, Alberta T3A 0A1 (CA). SPENCE, Rupert, Edward, von Haken [GB/CA]; 401 - 11 Street N.W., Calgary, Alberta T2N 1X5 (CA). BROWN, Stephen, John [CA/CA]; 157 Mount Sparrowhawk Place S.E., Calgary, Alberta T2Z 2G7 (CA). JEREMIC, Dusan [YU/CA]; 240 Sandstone Drive N.W., Calgary, Alberta T3K 3S6 (CA).</p> <p>(74) Agents: CHISHOLM, P., Scott et al.; Nova Chemicals Ltd., 2928 - 16 Street N.E., Calgary, Alberta T2E 7K7 (CA).</p>		
<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BG, BR, BY, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, JP, KE, KG, KP, KR, KZ, LK, LT, LV, MX, NO, NZ, PL, PT, RO, RU, SD, SG, SI, SK, TJ, TM, TR, UA, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>		
<p>(54) Title: CATALYST HAVING A KETIMIDE LIGAND</p> <p>(57) Abstract</p> <p>A catalyst system for olefin polymerization comprises an organometallic complex of a group 4 metal having a ketimide ligand. One of the preferred ketimide ligand is 'Bu₂C. The organometallic complex preferably also contains a cyclic ligand which forms a delocalized pi-bond with the metal (such as a cyclopentadienyl-type ligand). Preferred catalyst is: ('Bu₂C=N)TiCl₂Cp. Preferred organometallic complexes may be activated with a so-called "substantially non coordinating anion" (for example B(C₆F₅)₄) to form a low cost cocatalyst system which is excellent for the preparation of olefin copolymers having both high molecular weight and very low density.</p>		

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CATALYST HAVING A KETIMIDE LIGAND

TECHNICAL FIELD

This invention relates to a catalyst system for the preparation of olefin copolymers. The catalyst system is especially useful for the preparation of ethylene copolymers which have very high molecular weight and very low density. The catalyst system is characterized by the use of 10 an organometallic complex having a ketimide ligand.

BACKGROUND ART

Ketimide complexes of group 4 metals have been reported in the literature - see, for example, the review of titanium chemistry which was prepared in part by one of us in 1982 (Ref: M. Bottrill, P.D. Gavens, J.W. Kelland and J. McMeeking in "Comprehensive Organometallic Chemistry", Ed. G. Wilkinson, F.G.A. Stone, & E.W. Abel, Pergamon Press, 1982, Section 22.3, page 392). However, the use of ketimide ligand/group 4 20 metal complex as an ethylene polymerization catalyst was heretofore unknown.

Preferred ketimide catalysts of this invention also contain one and only one cyclopentadienyl-type ligand.

The prior art includes many examples of olefin polymerization catalysts having a single cyclopentadienyl ligand - most notably the so called Bercaw ligand ('Cp-Me₂Si-N'Bu) which was disclosed as a 30 Scandium complex by Bercaw *et al* in the fall of 1988 and subsequently claimed as a titanium complex in U.S. patents 5,064,802 (Stevens and Neithamer, to Dow Chemical) and 5,055,438 (Canich, to Exxon). The use of a titanium complex of the Bercaw ligand provides an olefin polymerization catalyst which has excellent comonomer response - i.e. the catalyst is excellent for the preparation of ethylene/α-olefin copolymers. However, the bridged structure of the Bercaw ligand is expensive to synthesize. Accordingly, an olefin polymerization catalyst which doesn't require a "bridge" to provide comonomer response would represent a useful addition to the art.

DISCLOSURE OF THE INVENTION

The present invention also provides a catalyst system for olefin polymerization comprising:

- (a) a catalyst which is an organometallic complex of a group 4 metal; and
- (b) an activator,

10 characterized in that such organometallic complex contains a ketimide ligand.

Preferred forms of the catalyst contain a single ketimide ligand and a single cyclopentadienyl-type ligand.

The invention further provides a process for the copolymerization of ethylene with at least one other olefin monomer using the above described catalyst system.

BEST MODE FOR CARRYING OUT THE INVENTION

The term "group 4" metal refers to conventional IUPAC nomenclature. The preferred group 4 metals are Ti, Hf and Zr with Ti being most preferred.

As used herein, the term "ketimide ligand" refers to a ligand which:

- (a) is bonded to the group 4 metal via a metal-nitrogen atom bond;
- (b) has a single substituent on the nitrogen atom, (where this single substituent is a carbon atom which is doubly bonded to the N atom); and
- (c) has two substituents (Sub 1 and Sub 2, described below) which are bonded to the carbon atom.

30 Conditions a, b, and c are illustrated below:

Sub 1 Sub 2



The substituents "Sub 1 and Sub 2" may be the same or different. Exemplary substituents include hydrocarbyls having from 1 to 20 carbon atoms; silyl groups, amido groups and phosphido groups. For reasons of cost and convenience it is preferred that these substituents both be hydrocarbyls, especially simple alkyls and most preferably tertiary butyl.

In the preferred catalyst systems, the catalyst is defined by the formula:

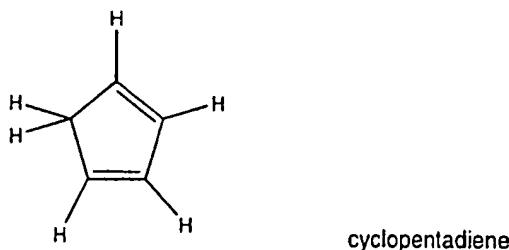
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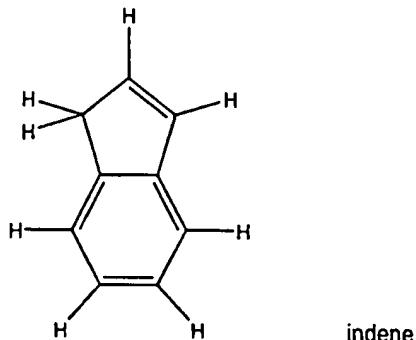
L2:

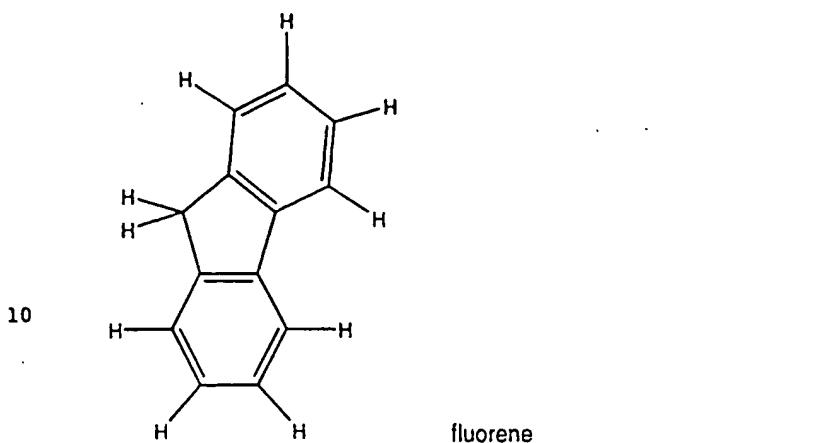
L2 is a cyclic ligand which forms a delocalized pi-bond with the group 4 metal. L2 is preferably a cyclopentadienyl-type ligand. As used herein, the term cyclopentadienyl-type is meant to convey its conventional meaning and to include indenyl and fluorenyl ligands. The simplest (unsubstituted) cyclopentadiene, indene and fluorene structures are illustrated below.

20



30





Ligands in which one of the carbon atoms in the ring is replaced with a phosphorous atom (i.e. a phosphole) may also be employed.

It will be readily appreciated by those skilled in the art that the hydrogen atoms shown in the above formula may be replaced with 20 substituents to provide the "substituted" analogues. Thus, the preferred catalysts contain a cyclopentadienyl structure which may be an unsubstituted cyclopentadienyl, substituted cyclopentadienyl, unsubstituted indenyl, substituted indenyl, unsubstituted fluorenyl or substituted fluorenyl. A description of permissible substituents on these cyclopentadienyl-type structures is provided in United States Patent 5,324,800 (Welborn).

An illustrative list of such substituents for cyclopentadienyl groups 30 included C₁-C₂₀ hydrocarbyl radicals; substituted C₁-C₂₀ hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical or a radical containing a Lewis acidic or basic functionality; substituted C₁-C₂₀ hydrocarbyl radicals wherein the substituent contains an atom selected from the group 14 of the Periodic Table of Elements (where group 14 refers to IUPAC nomenclature); and halogen radicals, amido radicals, phosphido radicals, alkoxy radicals, alkyborido radicals, or a radical containing Lewis acidic or basic functionality; or a ring in which two

adjacent R-groups are joined forming C₁-C₂₀ ring to give a saturated or unsaturated polycyclic ligand.

Ligand X: "Non-Interfering Anionic Ligand"

Referring for formula 1, the preferred catalyst systems according to this invention contain two simple anionic ligands denoted by the letter X.

Any simple anionic ligand which may be bonded to an analogous metallocene catalyst component ((i.e. where the analogous metallocene catalyst component is defined by the formula Cp₂M(X)₂, where Cp is a cyclopentadienyl-type ligand; M is a group 4 metal; and X is a non-interfering ligand is previously defined herein) may also be used with the catalyst components of this invention.

"Non-interfering" means that this ligand doesn't interfere with (deactivate) the catalyst.

An illustrative list includes hydrogen, hydrocarbyl having up to 10 carbon atoms, halogen, amido and phosphido (with each X preferably being chlorine, for simplicity).

Polymerization Details

The polymerization process of this invention is conducted in the presence of a catalyst and an "activator or cocatalyst". The terms "activator" or "cocatalyst" may be used interchangeably and refer to a catalyst component which combines with the organometallic complex to form a catalyst system that is active for olefin polymerization.

Preferred cocatalysts are the well known alumoxane (also known as aluminoxane) and ionic activators.

The term "alumoxane" refers to a well known article of commerce which is typically represented by the following formula:



where each R' is independently selected from alkyl, cycloalkyl, aryl or alkyl substituted aryl and has from 1-20 carbon atoms and where m is from 0 to about 50 (especially from 10 to 40). The preferred alumoxane is methylalumoxane or "MAO" (where each of the R' is methyl).

Alumoxanes are typically used in substantial molar excess compared to the amount of metal in the catalyst. Aluminum:transition metal molar ratios of from 10:1 to 10,000:1 are preferred, especially from 50:1 to 500:1.

Another type of activator is the "ionic activator" or "substantially non-coordinating anion". As used herein, the term substantially non-coordinating anions ("SNCA") well known cocatalyst or activator systems 10 which are described, for example, in United States Patent 5,153,157 (Hlatky and Turner), and the carbonium, sulfonium and oxonium analogues of such activators which are disclosed by Ewen in United States Patent 5,387,568. In general, these SNCA form an anion which only weakly coordinates to a cationic form of the catalyst.

While not wanting to be bound by theory, it is generally believed that SNCA-type activators ionize the catalyst by abstraction or protonation of one of the "X" ligands (non-interfering ligands) so as to ionize the group 20 4 metal center into a cation (but not to covalently bond with the group 4 metal) and to provide sufficient distance between the ionized group 4 metal and the activator to permit a polymerizable olefin to enter the resulting active site. It will be appreciated by those skilled in the art that it is preferable that the "non-interfering" ("X") ligands be simple alkyls when using a SNCA as the activator. This may be achieved by the alkylation of a halide form of the catalyst.

Examples of compounds capable of ionizing the group 4 metal complex include the following compounds:

30 triethylammonium tetra(phenyl)boron,
tripropylammonium tetra(phenyl)boron,
tri(n-butyl)ammonium tetra(phenyl)boron,
trimethylammonium tetra(p-tolyl)boron,
trimethylammonium tetra(o-tolyl)boron,
tributylammonium tetra(pentafluorophenyl)boron,
tripropylammonium tetra(o,p-dimethylphenyl)boron,
tributylammonium tetra(m,m-dimethylphenyl)boron,

tributylammonium tetra(p-trifluoromethylphenyl)boron,
tributylammonium tetra(pentafluorophenyl)boron,
tri(n-butyl)ammonium tetra (o-tolyl)boron,
N,N-dimethylanilinium tetra(phenyl)boron,
N,N-diethylanilinium tetra(phenyl)boron,
N,N-diethylanilinium tetra(phenyl)n-butylboron,
N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron,
10 di-(isopropyl)ammonium tetra(pentafluorophenyl)boron,
dicyclohexylammonium tetra(phenyl)boron,
triphenylphosphonium tetra(phenyl)boron,
tri(methylphenyl)phosphonium tetra(phenyl)boron,
tri(dimethylphenyl)phosphonium tetra(phenyl)boron,
tropillium tetrakis(pentafluorophenyl) borate,
triphenylmethylium tetrakis(pentafluorophenyl) borate,
benzene (diazonium) tetrakis(pentafluorophenyl) borate,
20 tropillium phenyltris-pentafluorophenyl borate,
triphenylmethylium phenyl-tris(pentafluorophenyl) borate,
benzene (diazonium) phenyltris(pentafluorophenyl) borate,
tropillium tetrakis (2,3,5,6-tetrafluorophenyl) borate,
triphenylmethylium tetrakis (2,3,5,6-tetrafluorophenyl) borate,
benzene (diazonium) tetrakis (3,4,5-trifluorophenyl) borate,
tropillium tetrakis (3,4,5-trifluorophenyl) borate,
benzene (diazonium) tetrakis (3,4,5-trifluorophenyl) borate,
tropillium tetrakis (1,2,2-trifluoroethenyl) borate,
30 tropillium methylium tetrakis (1,2,2-trifluoroethenyl) borate,
benzene (diazonium) tetrakis (1,2,2-trifluoroethenyl) borate,
tropillium tetrakis (2,3,4,5-tetrafluorophenyl) borate,
triphenylmethylium tetrakis (2,3,4,5-tetrafluorophenyl) borate,
and
benzene (diazonium) tetrakis (2,3,4,5-tetrafluorophenyl) borate.

Readily commercially available activators which are capable of ionizing the group 4 metal complexes include:

N,N-dimethylaniliniumtetrakis(pentafluorophenyl) borate

("[Me₂NHPh][B(C₆F₅)₄]"); and

triphenylmethylium tetrakis(pentafluorophenyl) borate

("[Ph₃C][B(C₆F₅)₄]"); and

tris(pentafluorophenyl) boron.

These SNCA activators are typically used in approximately

10 equimolar amounts (based on the group 4 metal in the catalyst) but lower levels may also be successful and higher levels also generally work (though sub-optimally with respect to the cost-effective use of the expensive activator).

In addition to the catalyst and cocatalyst, the use of a "poison scavenger" may also be desirable. As may be inferred from the name "poison scavenger", these additives may be used in small amounts to scavenge impurities in the polymerization environment. Aluminum alkyls, for example triisobutyl aluminum, are suitable poison scavengers. (Note: 20 some caution must be exercised when using poison scavengers as they may also react with, and deactivate, the catalyst.)

Polymerizations according to this invention may be undertaken in any of the well known olefin polymerization processes including those known as "gas phase", "slurry", "high pressure" and "solution".

The use of a supported catalyst is preferred for gas phase and slurry processes whereas a non-supported catalyst is preferred for the solution process.

When utilizing a supported catalyst, it may be preferable to initially 30 support the cocatalyst, then the catalyst (as will be illustrated in the Examples).

The polymerization process according to this invention uses ethylene and may include other monomers which are copolymerizable therewith (such as other alpha olefins, preferably butene, hexene or octene, and under certain conditions, dienes such as hexadiene isomers, vinyl aromatic monomers such as styrene or cyclic olefin monomers such as norbornene).

The present invention may also be used to prepare elastomeric co- and terpolymers of ethylene, propylene and optionally one or more diene monomers. Generally, such elastomeric polymers will contain about 50 to about 75 weight % ethylene, preferably about 50 to 60 weight % ethylene and correspondingly from 50 to 25 % of propylene. A portion of the monomers, typically the propylene monomer, may be replaced by a conjugated diolefin. The diolefin may be present in amounts up to 10 weight % of the polymer although typically is present in amounts from about 3 to 5 weight %. The resulting polymer may have a composition comprising from 40 to 75 weight % of ethylene, from 50 to 15 weight % of propylene and up to 10 weight % of a diene monomer to provide 100 weight % of the polymer. Preferred but not limiting examples of the dienes are dicyclopentadiene, 1,4-hexadiene, 5-methylene-2-norbornene, 5-ethylidene-2-norbornene and 5-vinyl-2-norbornene. Particularly preferred dienes are 5-ethylidene-2-norbornene and 1,4-hexadiene.

20 The polyethylene polymers which may be prepared in accordance with the present invention typically comprise not less than 60, preferably not less than 70 weight % of ethylene and the balance one or more C₄-₁₀ alpha olefins, preferably selected from the group consisting of 1-butene, 1-hexene and 1-octene. The polyethylene prepared in accordance with the present invention may be linear low density polyethylene having density from about 0.910 to 0.935 g/cc. The present invention might also be useful to prepare polyethylene having a density below 0.910 g/cc - the so called very low and ultra low density polyethylenes.

30 The most preferred polymerization process of this invention encompasses the use of the novel catalysts (together with a cocatalyst) in a medium pressure solution process. As used herein, the term "medium pressure solution process" refers to a polymerization carried out in a solvent for the polymer at an operating temperature from 100 to 320°C (especially from 120 to 220°C) and a total pressure of from 3 to 35 mega Pascals. Hydrogen may be used in this process to control (reduce) molecular weight. Optimal catalyst and cocatalyst concentrations are

affected by such variables as temperature and monomer concentration but may be quickly optimized by non-inventive tests.

Further details concerning the medium pressure polymerization process are well known to those skilled in the art and widely described in the open and patent literature.

The catalyst of this invention may also be used in a slurry polymerization process or a gas phase polymerization process.

10 The typical slurry polymerization process uses total reactor pressures of up to about 50 bars and reactor temperature of up to about 200°C. The process employs a liquid medium (e.g. an aromatic such as toluene or an alkane such as hexane, propane or isobutane) in which the polymerization take place. This results in a suspension of solid polymer particles in the medium. Loop reactors are widely used in slurry processes. Detailed descriptions of slurry polymerization processes are widely reported in the open and patent literature.

20 In general, a fluidized bed gas phase polymerization reactor employs a "bed" of polymer and catalyst which is fluidized by a flow of monomer which is at least partially gaseous. Heat is generated by the enthalpy of polymerization of the monomer flowing through the bed. Unreacted monomer exits the fluidized bed and is contacted with a cooling system to remove this heat. The cooled monomer is then re-circulated through the polymerization zone together with "make-up" monomer to replace that which was polymerized on the previous pass. As will be appreciated by those skilled in the art, the "fluidized" nature of the

30 polymerization bed helps to evenly distribute/mix the heat of reaction and thereby minimize the formation of localized temperature gradients (or "hot spots"). Nonetheless, it is essential that the heat of reaction be properly removed so as to avoid softening or melting of the polymer (and the resultant-and highly undesirable - "reactor chunks"). The obvious way to maintain good mixing and cooling is to have a very high monomer flow through the bed. However, extremely high monomer flow causes undesirable polymer entrainment.

An alternative (and preferable) approach to high monomer flow is the use of an inert condensable fluid which will boil in the fluidized bed (when exposed to the enthalpy of polymerization), then exit the fluidized bed as a gas, then come into contact with a cooling element which condenses the inert fluid. The condensed, cooled fluid is then returned to the polymerization zone and the boiling/condensing cycle is repeated.

10 The above-described use of a condensable fluid additive in a gas phase polymerization is often referred to by those skilled in the art as "condensed mode operation" and is described in additional detail in USP 4,543,399 and USP 5,352,749. As noted in the '399 reference, it is permissible to use alkanes such as butane, pentanes or hexanes as the condensable fluid and the amount of such condensed fluid preferably does not exceed about 20 weight per cent of the gas phase.

Other reaction conditions for the polymerization of ethylene which are reported in the '399 reference are:

20 Preferred Polymerization Temperatures: about 75°C to about 115°C (with the lower temperatures being preferred for lower melting copolymers - especially those having densities of less than 0.915 g/cc - and the higher temperatures being preferred for higher density copolymers and homopolymers); and Pressure: up to about 1000 psi (with a preferred range of from about 100 to 350 psi for olefin polymerization).

30 The '399 reference teaches that the fluidized bed process is well adapted for the preparation of polyethylene but further notes that other monomers may also be employed. The present invention is similar with respect to choice of monomers.

Catalysts which are used in gas phase and slurry polymerizations are preferably supported. An exemplary list of support materials include metal oxides (such as silica, alumina, silica-alumina, titania and zirconia); metal chlorides (such as magnesium chloride); talc, polymers (including polyolefins); partially prepolymerized mixtures of a group 4 metal complex, activator and polymer; spray dried mixtures of the group 4 metal complex,

activator and fine "inert" particles (as disclosed, for example, in European Patent Office Application 668,295 (to Union Carbide).

The preferred support material is silica. In a particularly preferred embodiment, the silica has been treated with an alumoxane (especially methylalumoxane or "MAO") prior to the deposition of the group 4 metal complex. The procedure for preparing "supported MAO" which is described in USP 5,534,474 (to Witco) may provide a low cost catalyst support. It will be recognized by those skilled in the art that silica may be characterized by such parameters as particle size, pore volume and residual silanol concentration. The pore size and silanol concentration may be altered by heat treatment or calcining. The residual silanol groups provide a potential reaction site between the alumoxane and the silica (and, indeed, some off gassing is observed when alumoxane is reacted with silica having residual silanol groups). This reaction may help to "anchor" the alumoxane to the silica (which, in turn, may help to reduce reactor fouling).

The preferred particle size, preferred pore volume and preferred residual silanol concentration may be influenced by reactor conditions. Typical silicas are dry powders having a particle size of from 1 to 200 microns (with an average particle size of from 30 to 100 being especially suitable); pore size from 50 to 500 Angstroms; and pore volumes of from 0.5 to 5.0 cubic centimeters per gram. As a general guideline, the use of commercially available silicas, such as those sold by W.R. Grace under the trademarks Davison 948 or Davison 955, are suitable.

EXAMPLES

The invention will now be illustrated in further detail by way of the following non-limiting examples. For clarity, the Examples have been divided into two parts, namely Part A (Catalyst Component Synthesis), Part B (Solution Polymerization) and Part C (Gas Phase Polymerization).

Polymer Analysis

Gel permeation chromatography ("GPC") analysis was carried out using a commercially available chromatograph (sold under the name

Waters 150 GPC) using 1,2,4-trichlorobenzene as the mobile phase at 140°C. The samples were prepared by dissolving the polymer in the mobile phase solvent in an external oven at 0.1% (weight/volume) and were run without filtration. Molecular weights are expressed as polyethylene equivalents with a relative standard deviation of 2.9% and 5.0% for the number average molecular weight M_n and weight M_w , respectively. Melt index (MI) measurements were conducted according to 10 ASTM method D-1238-82.

Polymer densities were measured using pressed plaques (AST D-1928-90), with a densitometer. The polymer composition was determined using FTIR where the 1-butene or 1-hexene content was measured.

Part A: Catalyst Component Synthesis

Experimental Section

Catalyst components were prepared using conventional organometallic synthetic techniques, as described below.

20 **Preparation of $^1\text{Bu}_2\text{C}=\text{NLi}$ (where ^1Bu is tertiary butyl, and $^1\text{Bu}_2$ shows that two tertiary butyl groups are bonded to the C (carbon) atom)**

This compound was prepared according to a published procedure, D. Armstrong, D. Barr and R. Sanith J. Chem. Soc. Dalton Trans. 1987, 1071. ^1H NMR (proton nuclear magnetic resonance) (toluene- d_6 , δ): 1.21 (s).

Synthesis of $(^1\text{Bu}_2\text{C}=\text{N})\text{TiCl}_2\text{Cp}$ (where Cp is a cyclopentadienyl ligand)

30 A solution of $^1\text{Bu}_2\text{C}=\text{NLi}$ (1.34 g, 9.11 mmol) in toluene (~20 mL, i.e. approximately 20 mL) was added slowly to CpTiCl_3 (2.0 g, 9.11 mmol) in toluene (~30 mL) at -78°C. The yellow solution became orange immediately. The reaction mixture was warmed to 23°C in 12 hours. The reddish purple solution was filtered through a fine glass filter to remove LiCl and the filtrate was pumped to ~5 mL and hexane (~40 mL) was added. The product crystallized at -70°C as purple crystals (2.4 g). Evaporation of the mother liquor in a glove box gave X-ray quality crystals

(extra 0.3 g). The combined yield was 91%. ^1H NMR (toluene- d_6 , δ): 6.12 (s, 5H), 1.04 (s, 18H).

Synthesis of ($^1\text{Bu}_2\text{C}=\text{N}$) TiMe_2Cp (where Me is methyl)

MeMgBr (3M in ether; 1.1 mL, 3.3 mmol) was added to a toluene solution (40 mL) of ($^1\text{Bu}_2\text{C}=\text{N}$) TiCl_2Cp (0.416g, 1.283 mmol) at -78°C. After the addition, the solution was warmed to 23°C in 30 minutes and was then pumped to dryness. The residue was extracted with hexane (2x35 mL) and the slurry was filtered. The filtrate was pumped to dryness to give the pure product as an orange oil. ^1H NMR (toluene- d_6 , δ): 6.0 (s, 5H), 1.15 (s, 18H), 0.636 (s, 6H).

Synthesis of ($^1\text{Bu}_2\text{C}=\text{N}$) TiCl_2Cp^* (where Cp^* is pentamethylcyclopentadienyl)

Analogous to the synthesis of ($^1\text{Bu}_2\text{C}=\text{N}$) TiCl_2Cp , this compound was synthesized from $^1\text{Bu}_2\text{C}=\text{NLi}$ and Cp^*TiCl_3 as orange crystals in almost quantitative yield. ^1H NMR (toluene- d_6 , δ): 1.976 (s, 15H), 1.15 (s, 18H).

Synthesis of ($^1\text{Bu}_2\text{C}=\text{N}$) TiMe_2Cp^*

Analogous to the synthesis of ($^1\text{Bu}_2\text{C}=\text{N}$) TiMe_2Cp , this compound was prepared from MeMgBr and ($^1\text{Bu}_2\text{C}=\text{N}$) TiCl_2Cp^* as orange crystals in quantitative yield. ^1H NMR (toluene- d_6 , δ): 1.889(s, 15H), 1.219 (s, 18H), 0.446(s, 6H).

Synthesis of $[(\text{Me}_2\text{N})_2\text{C}=\text{N}]\text{TiCl}_2\text{Cp}$

BuLi (1.6 M in hexane, 6.25 mL, 10 mmol) was added to a toluene solution (~15 mL) of $(\text{Me}_2\text{N})_2\text{C}=\text{NH}$ (1.151g, 10 mmol) at -78°C. The solution was warmed to 23°C in 10 minutes and was further stirred for 30 minutes to give a toluene solution of $(\text{Me}_2\text{N})_2\text{C}=\text{NLi}$ (10 mmol).

The above solution was added to a toluene solution (~50 mL) of CpTiCl_3 (2.19 g, 10 mmol) at -78°C. The mixture was warmed to 23°C in the cold bath. Yellow precipitate was observed. The slurry was pumped to dryness and the residue was extracted with dichloromethane (50 mL). The dichloromethane solution was filtered and was concentrated to ~10

mL. The product crystallized at -20°C as bright orange crystals after hexane (30 mL) was added. Yield was 2.8 g, 94%. ¹H NMR (toluene-d₆, δ): 6.28 (s, 5H), 2.26 (s, 12H).

Synthesis of (Bu₂C=N)TiCl₂(C₄Me₄P) (where C₄Me₄P is tetramethylphospholyl)

10 ¹Bu₂C=NLi (0.384 g, 2.610 mmol) in toluene (-20 mL) was added into a toluene solution (~30 mL) of (C₄Me₄P)TiCl₃ (0.766g, 2.610 mmol). The reaction was warmed to 23°C in 5 hours. The solution was filtered and the filtrate was pumped to dryness. The residue was crystallized from hexane at -70°C (0.920 g, 96%) as orange crystals. ¹H NMR (toluene-d₆, δ): 2.18 (d, J = 9.9 Hz, 6H), 2.03 (s, 6H), 1.17 (s, 18H).

Synthesis of (Bu₂C=N)TiMe₂(C₄Me₄P)

20 This compound was prepared as orange crystals in quantitative yield from the reaction of (Bu₂C=N)TiCl₂(C₄Me₄P) and excess of MeMgBr (Procedure was similar to that for the preparation of (Bu₂C=N)TiMe₂Cp). ¹H NMR (toluene-d₆, δ): 2.02 (d, J = 10 Hz, 6H), 1.94 (s, 6H), 0.55 (d, J = 0.95 Hz, 6H).

Synthesis of [Ph(Me)C=N]TiMe₂Cp (where Ph is phenyl; Me is methyl)

MeLi (1.4 M in ether, 7.14 mL, 10 mmol) was added to PhCN (1.03 g, 10 mmol) in ether (~30 mL) at -100°C. The solution was warmed to 23°C in 0.5 hr and was stirred for another 0.5 hours. An orange solution of Ph(Me)C=NLi formed.

30 The above solution was added to a solution of CpTiCl₃ in ether (~100 mL) at -78°C and the reaction mixture was warmed to 23°C in ~1 hour. The orange solution was pumped to dryness and the residue was extracted with toluene. The toluene solution was filtered and was concentrated to ~2 mL. The product crystallized from a mixture of toluene and hexane at -70°C. Yield 2.93, 97%. ¹H NMR (toluene-d₆, δ): 6.9-7.6 (m, 5H), 6.14 (s, 5H), 1.84 (s, 3H).

Synthesis of (¹Bu₂C=N)TiCl₂(Ind) (where Ind is indenyl)

A solution of ¹Bu₂C=NLi (0.332 g, 2.17 mmol) in 30 mL of toluene was added dropwise to IndTiCl₃ (0.584 g, 2.17 mmol) in 30 mL of toluene at -78°C. Once the addition was complete the solution was allowed to reach room temperature while being stirred for 16 hours. The purple solution was then filtered to remove LiCl and toluene was removed under reduced pressure to give a dark purple crystalline solid. Isolated yield is 10 0.681 g (83%). ¹H NMR (toluene-d₆, δ) (C₇D₆): 7.25 (m, 2H), 6.88 (m, 2H), 6.44 (m, 3H), 1.01 (s, 18H).

Part B: Solution Polymerization**The Continuous Solution Polymerization**

All the polymerization experiments described below were conducted on a continuous solution polymerization reactor. The process is continuous in all feed streams (solvent, monomers and catalyst) and in the removal of product. All feed streams were purified prior to the reactor 20 by contact with various absorption media to remove catalyst killing impurities such as water, oxygen and polar materials as is known to those skilled in the art. All components were stored and manipulated under an atmosphere of purified nitrogen.

All the examples below were conducted in a reactor of 71.5 cc internal volume. In each experiment the volumetric feed to the reactor was kept constant and as a consequence so was the reactor residence time.

The catalyst solutions were pumped to the reactor independently 30 and there was no pre-contact between the activator and the catalyst. Because of the low solubility of the catalysts, activators and MAO in cyclohexane, solutions were prepared in purified xylene. The catalyst was activated *in-situ* (in the polymerization reactor) at the reaction temperature in the presence of the monomers. The polymerizations were carried out in cyclohexane at a pressure of 1500 psi. Ethylene was supplied to the reactor by a calibrated thermal mass flow meter and was dissolved in the reaction solvent prior to the polymerization reactor. If comonomer (for

example 1-octene) was used it was also premixed with the ethylene before entering the polymerization reactor. Under these conditions the ethylene conversion is a dependent variable controlled by the catalyst concentration, reaction temperature and catalyst activity, etc.

The internal reactor temperature is monitored by a thermocouple in the polymerization medium and can be controlled at the required set point to +/- 0.5°C. Downstream of the reactor the pressure was reduced from the reaction pressure (1500 psi) to atmospheric. The solid polymer was then recovered as a slurry in the condensed solvent and was dried by evaporation before analysis.

The ethylene conversion was determined by a dedicated on line gas chromatograph by reference to propane which was used as an internal standard. The average polymerization rate constant was calculated based on the reactor hold-up time, the catalyst concentration in the reactor and the ethylene conversion and is expressed in l/(mmol¹min).

Average polymerization rate (k_p) = $(Q/(100-Q)) \times (1/[M]) \times (1/HUT)$:

where: Q is the percent ethylene conversion;

$[M]$ is the catalyst (metal) concentration in the reactor expressed in mM; and

HUT is the reactor hold-up time in minutes.

Example 1

$^{1\prime}Bu_2C=N)TiCl_2Cp$ was added to the reactor at 37×10^{-6} mol/l along with MAO (PMAO-IP, Akzo-Nobel) at Al/Ti = 200. [Note: all Al/Ti ratios referred to in the Examples are mol/mol basis)]. The reaction temperature was 160°C and 2.1 gram/min. of ethylene was continuously added to the reactor. An ethylene conversion of 37.5% was observed (see Table 1).

Example 2

$^{1\prime}Bu_2C=N)TiCl_2Cp$ was added to the reactor at 37×10^{-6} mol/l along with MAO (PMAO-IP, Akzo-Nobel) at Al/Ti = 200 (mol/mol). The reaction temperature was 160°C, 2.1 gram/min. of ethylene and 4.0 ml/min. of 1-octene was continuously added to the reactor. An ethylene conversion of 28.5% was observed (see Table 1).

Example 3

$(^1\text{Bu}_2\text{C}=\text{N})\text{TiMe}_2\text{Cp}$ was added to the reactor at 37×10^{-6} mol/l along with $\text{Ph}_3\text{C B}(\text{C}_6\text{F}_5)_4$ (Asahi Glass) at $\text{B/Ti} = 1.0$ (mol/mol). The reaction temperature was 160°C and 2.1 gram/min. of ethylene was continuously added to the reactor. An ethylene conversion of 58.7% was observed (see Table 1).

Example 4

10 $(^1\text{Bu}_2\text{C}=\text{N})\text{TiMe}_2\text{Cp}$ was added to the reactor at 18.5×10^{-6} mol/l along with $\text{Ph}_3\text{C B}(\text{C}_6\text{F}_5)_4$ (Asahi Glass) at $\text{B/Ti} = 1.0$ (mol/mol). The reaction temperature was 160°C and 2.1 gram/min. of ethylene was continuously added to the reactor. An ethylene conversion of 51.6% was observed (see Table 1).

Example 5

20 $(^1\text{Bu}_2\text{C}=\text{N})\text{TiMe}_2\text{Cp}$ was added to the reactor at 37×10^{-6} mol/l along with $\text{Ph}_3\text{C B}(\text{C}_6\text{F}_5)_4$ (Asahi Glass) at $\text{B/Ti} = 1.0$ (mol/mol). The reaction temperature was 160°C and 2.1 gram/min. of ethylene along with 4.0 ml/min. of purified 1-octene was continuously added to the reactor. An ethylene conversion of 45.5% was observed (see Table 1).

Example 6

30 $(^1\text{Bu}_2\text{C}=\text{N})\text{TiCl}_2\text{Cp}^*$ was added to the reactor at 37×10^{-6} mol/l along with MAO (PMAO-IP, Akzo-Nobel) at $\text{Al/Ti} = 200$ (mol/mol). The reaction temperature was 160°C and 2.1 gram/min. of ethylene was continuously added to the reactor. An ethylene conversion of 78.7% was observed (see Table 1).

Example 7

$(^1\text{Bu}_2\text{C}=\text{N})\text{TiCl}_2\text{Cp}^*$ was added to the reactor at 37×10^{-6} mol/l along with MAO (PMAO-IP, Akzo-Nobel) at $\text{Al/Ti} = 200$ (mol/mol). The reaction temperature was 160°C , 2.1 gram/min. of ethylene and 4.0 ml/min. of 1-octene was continuously added to the reactor. An ethylene conversion of 60.3% was observed (see Table 1).

Example 8

$(^1\text{Bu}_2\text{C}=\text{N})\text{TiCl}_2\text{Cp}^*$ was added to the reactor at 37×10^{-6} mol/l along with MAO (PMAO-IP, Akzo-Nobel) at Al/Ti = 200 (mol/mol). The reaction temperature was 160°C, 2.1 gram/min. of ethylene along with 2.0 ml/min. of purified 1-octene was continuously added to the reactor. An ethylene conversion of 66.9% was observed (see Table 1).

Example 9

10 $(^1\text{Bu}_2\text{C}=\text{N})\text{TiMe}_2\text{Cp}^*$ was added to the reactor at 37×10^{-6} mol/l along with $\text{Ph}_3\text{C B}(\text{C}_6\text{F}_5)_4$ (Asahi Glass) at B/Ti = 1.0 (mol/mol). The reaction temperature was 160°C, 2.1 gram/min. of ethylene was continuously added to the reactor. An ethylene conversion of 81.4% was observed (see Table 1).

Example 10

20 $(^1\text{Bu}_2\text{C}=\text{N})\text{TiMe}_2\text{Cp}^*$ was added to the reactor at 37×10^{-6} mol/l along with $\text{Ph}_3\text{C B}(\text{C}_6\text{F}_5)_4$ (Asahi Glass) at B/Ti = 1.0 (mol/mol). The reaction temperature was 160°C, 2.1 gram/min. of ethylene and 4.0 ml/min. of 1-octene was continuously added to the reactor. An ethylene conversion of 60.8% was observed (see Table 1).

Example 11

30 $(^1\text{Bu}_2\text{C}=\text{N})\text{TiMe}_2\text{Cp}^*$ was added to the reactor at 37×10^{-6} mol/l along with $\text{Ph}_3\text{C B}(\text{C}_6\text{F}_5)_4$ (Asahi Glass) at B/Ti = 1.0 (mol/mol). The reaction temperature was 140°C, 1.0 gram/min. of ethylene was continuously added to the reactor. An ethylene conversion of 94.3% was observed (see Table 1).

Example 12

$(^1\text{Bu}_2\text{C}=\text{N})\text{TiCl}_2(\text{C}_4\text{Me}_4\text{P})$ was added to the reactor at 37×10^{-6} mol/l along with $\text{Ph}_3\text{C B}(\text{C}_6\text{F}_5)_4$ (Asahi Glass) at B/Ti = 1.0 (mol/mol). The reaction temperature was 160°C, 2.1 gram/min. of ethylene was continuously added to the reactor. An ethylene conversion of 34.5% was observed (see Table 1).

Example 13

$(^1\text{Bu}_2\text{C}=\text{N})\text{TiCl}_2(\text{C}_4\text{Me}_4\text{P})$ was added to the reactor at 148×10^{-6} mol/l along with $\text{Ph}_3\text{C B}(\text{C}_6\text{F}_5)_4$ (Asahi Glass) at $\text{B/Ti} = 1.0$ (mol/mol). The reaction temperature was 160°C , 2.1 gram/min. of ethylene and 3.0 ml/min. of 1-octene was continuously added to the reactor. An ethylene conversion of 46.1% was observed (see Table 1).

Comparative Example 14

10 $(\text{C}_5\text{Me}_5)_2\text{ZrCl}_2$ (purchased from Strem, where C_5Me_5 is pentamethylcyclopentadienyl) was added to the reactor at 37×10^{-6} mol/l along with MMAO-3 (Akzo-Nobel, $\text{Al/Ti} = 400$ mol/mol). The reaction temperature was 140°C and 1.0 gram/min. of ethylene was continuously added to the reactor. An ethylene conversion of 55.5% was observed (see Table 1).

Comparative Example 15

20 $(\text{C}_5\text{Me}_5)_2\text{ZrCl}_2$ (Strem) was added to the reactor at 37×10^{-6} mol/l along with MMAO-3 (Akzo-Nobel, $\text{Al/Ti} = 400$ mol/mol). The reaction temperature was 160°C and 1.0 gram/min. of ethylene was continuously added to the reactor. An ethylene conversion of 35.6% was observed (see Table 1).

Comparative Example 16

30 $(\text{C}_5\text{Me}_5)_2\text{ZrCl}_2$ (Strem) was added to the reactor at 37×10^{-6} mol/l along with MMAO-3 (Akzo-Nobel, $\text{Al/Ti} = 400$ mol/mol). The reaction temperature was 160°C and 2.1 gram/min. of ethylene was continuously added to the reactor. An ethylene conversion of 37.4% was observed (see Table 1).

Comparative Example 17

rac- $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ ((i.e. racemic form of ethylene bridged bis Indenyl ZrCl_2 , purchase from Witco) was added to the reactor at 37×10^{-6} mol/l along with MMAO-3 (Akzo-Nobel, $\text{Al/Ti} = 400$ mol/mol). The reaction temperature was 160°C and 2.1 gram/min. of ethylene was continuously added to the reactor. An ethylene conversion of 94.6% was observed (see Table 1).

Comparativ Exampl 18

rac-Et(Ind)₂ZrCl₂ (Witco) was added to the reactor at 37×10^{-6} mol/l along with MMAO-3 (Akzo-Nobel, Al/Ti = 400 mol/mol). The reaction temperature was 160°C and 2.1 gram/min. of ethylene and 3.25 ml/min. of 1-octene was continuously added to the reactor. An ethylene conversion of 94.8% was observed (see Table 1).

Example 19. Slurry Polymerization

10 Slurry polymerizations were carried out in a temperature controlled reactor at 35°C at an ethylene pressure of 10 psig. 300 ml of purified cyclohexane was first transferred to the reactor followed by MAO (PMAO-IP, Akzo-Nobel, 1.8 ml of 12.9 wt % Al) and was then stirred for 5 minutes. The catalyst ('Bu₂C=N)TiCl₂Cp (15.2 x 10⁻⁶ moles, to give a reactor concentration of 50×10^{-6} M, Al/Ti = 500) was then added and the reactor pressurized to 10 psig with ethylene. Polymerization was allowed to continue to 30 minutes at which time the pressure was vented (to prevent further reaction) and the polymer was recovered by evaporation of the solvent. Reactor temperature and ethylene consumption were monitored during the reaction. The polymer yield was 5.08 g giving an activity of 0.17 kg PE/(mmol Ti x hr).

Example 20. Slurry Polymerization

Reaction conditions were similar to those of example 19. MAO (PMAO-IP, Akzo-Nobel, 1.8 ml of 12.9 wt % Al) and ('Bu₂C=N)TiCl₂Cp* (15.2 x 10⁻⁶ moles, to give a reactor concentration of 50×10^{-6} M, Al/Ti = 500) were added and the reactor pressurized to 10 psig with ethylene. 30 The polymer yield was 6.26 g giving an activity of 0.21 kg PE/(mmol Ti x hr).

Example 21. Slurry Polymerization

Reaction conditions were similar to those of example 19. MAO (PMAO-IP, Akzo-Nobel, 1.8 ml of 12.9 wt % Al) and [(Me₂N)₂C=N]TiCl₂Cp (15.2 x 10⁻⁶ moles, to give a reactor concentration of 50×10^{-6} M, Al/Ti = 500) were added and the reactor pressurized to 10 psig with ethylene.

The polymer yield was 0.81 g giving an activity of 0.03 kg PE/(mmol Ti x hr).

Example 22. Slurry Polymerization

Reaction conditions were similar to those of example 19. MAO (PMAO-IP, Akzo-Nobel, 1.8 ml of 12.9 wt % Al) and ('Bu₂C=N)TiCl₂Ind (15.2 x 10⁻⁶ moles, to give a reactor concentration of 50 x 10⁻⁶ M, Al/Ti = 500) were added and the reactor pressurized to 10 psig with ethylene. The polymer yield was 13.02 g giving an activity of 0.43 kg PE/(mmol Ti x hr).

Example 23. Slurry Polymerization

Reaction conditions were similar to those of example 19. MAO (PMAO-IP, Akzo-Nobel, 1.8 ml of 12.9 wt % Al) and ('Bu₂C=N)TiCl₂(C₄Me₄P) (15.2 x 10⁻⁶ moles, to give a reactor concentration of 50 x 10⁻⁶ M, Al/Ti = 500) were added and the reactor pressurized to 10 psig with ethylene. The polymer yield was 2.63 g giving an activity of 0.09 kg PE/(mmol Ti x hr).

Comparative Example 24. Slurry polymerization

Reaction conditions were similar to those of example 19. MAO (PMAO-IP, Akzo-Nobel, 1.8 ml of 12.9 wt % Al) and [Ph(Me)C=N]TiMe₂Cp (15.2 x 10⁻⁶ moles, to give a reactor concentration of 50 x 10⁻⁶ M, Al/Ti = 500) were added and the reactor pressurized to 10 psig with ethylene. The polymer yield was 0.84 g giving an activity of 0.03 kg PE/(mmol Ti x hr).

Comparative Example 25. Slurry polymerization

Reaction conditions were similar to those of example 19. MAO (PMAO-IP, Akzo-Nobel, 1.8 ml of 12.9 wt % Al) and Ph₂C(Flu)(Cp)ZrCl₂ (15.2 x 10⁻⁶ moles, to give a reactor concentration of 50 x 10⁻⁶ M, Al/Ti = 500) were added and the reactor pressurized to 10 psig with ethylene. The polymer yield was 5.64 g giving an activity of 0.02 kg PE/(mmol Zr x hr).

Comparativ Exampl 26. Slurry polymerization

Reaction conditions were similar to those of example 19. MAO (PMAO-IP, Akzo-Nobel, 1.8 ml of 12.9 wt % Al) and $(Cp)_2ZrCl_2$ (15.2×10^{-6} moles, to give a reactor concentration of 50×10^{-6} M, Al/Ti = 500) were added and the reactor pressurized to 10 psig with ethylene. The polymer yield was 20.18 g giving an activity of 0.69 kg PE/(mmol Zr x hr).

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TABLE 1

Example	Total Flow To Reactor (ml/min.)	Catalyst Concentration (mol x 10 ⁶)	Ethylene Conversion (%)	Calculated Polymerization Rate (kp) (l/mmol x min.)	Polymer Density (g/cc)	Polymer Melt Index	Mn x 10 ³	Mw x 10 ³
1	27.0	37.0	37.5	6.2	0.958	0.08	52	174
2	27.0	37.0	28.5	4.1	0.920	0.452	43	128
3	27.0	37.0	58.7	14.5	-	-	-	-
4	27.0	18.0	51.6	21.8	0.9371	<0.001	227	448
5	27.0	37.0	45.5	8.5	0.8965	0.003	-	-
6	27.0	37.0	78.7	37.7	0.951	0.04	113	218
7	27.0	37.0	60.3	15.5	0.906	0.078	77	184
8	27.0	37.0	66.9	20.6	0.913	0.042	-	-
9	27.0	37.0	81.4	44.7	-	-	-	-
10	27.0	37.0	60.8	15.8	0.8888	0.100	-	-
11	27.0	37.0	94.3	169.6	0.942	0.023	-	-
12	27.0	37.0	34.5	5.4	-	-	-	-
13	27.0	148.1	46.1	2.2	0.906	0.007	63	288
14	27.0	37.0	55.5	12.7	-	880	2.7	10.0
15	27.0	37.0	35.6	5.6	-	-	1.8	7.5
16	27.0	37.0	37.4	6.1	-	620	3.3	12.0
17	27.0	37.0	94.6	178.6	-	1300	3.9	14.0
18	27.0	37.0	94.8	186.0	0.925	very high	2.6	10.0

Part C: Gas Phase Polymerization**Catalyst Preparation and Polymerization Testing Using a Semi-Batch, Gas Phase Reactor**

The catalyst preparation methods described below employ typical techniques for the syntheses and handling of air-sensitive materials.

Standard Schlenk and drybox techniques were used in the preparation of 10 ligands, metal complexes, support substrates and supported catalyst systems. Solvents were purchased as anhydrous materials and further treated to remove oxygen and polar impurities by contact with a combination of activated alumina, molecular sieves and copper oxide on silica/alumina. Where appropriate, elemental compositions of the supported catalysts were measured by Neutron Activation analysis and a reported accuracy of $\pm 1\%$ (weight basis).

The supported catalysts were prepared by initially supporting MAO on a 20 silica support, followed by deposition of the catalyst component.

All the polymerization experiments described below were conducted using a semi-batch, gas phase polymerization reactor of total internal volume of 2.2 L. Reaction gas mixtures, including separately ethylene or ethylene/butene mixtures were measured to the reactor on a continuous basis using a calibrated thermal mass flow meter, following passage through purification media as described above. A pre-determined mass of the catalyst sample was added to the reactor under the flow of the inlet gas with no pre-contact of the catalyst with any reagent, 30 such as a catalyst activator. The catalyst was activated *in-situ* (in the polymerization reactor) at the reaction temperature in the presence of the monomers, using a metal alkyl complex which has been previously added to the reactor to remove adventitious impurities. Purified and rigorously anhydrous sodium chloride was used as a catalyst dispersing agent.

The internal reactor temperature is monitored by a thermocouple in the polymerization medium and can be controlled at the required set point to $\pm 1.0^\circ\text{C}$. The duration of the polymerization experiment was one hour.

Following the completion of the polymerization experiment, the polymer was separated from the sodium chloride and the yield determined.

Table 2 illustrates data concerning the Al/transition metal ratios of the supported catalyst; polymer yield and polymer properties.

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TABLE 2

Complex	mmol Complex	Support ¹ (g)	mg of Catalyst	Homo ² or Co ² (g)	Yield	g Pe ³ /g Metal	g Pe ³ /g	Al/Ti Ratio
(<i>t</i> Bu ₂ C=N)TiCl ₂ Cp	52 mg (160 mmol)	1.485	48	Homo	2.6	5710	54	86.00
(<i>t</i> Bu ₂ C=N)TiCl ₂ Cp [*]	45 mg (114 mmol)	1.031	51	Co	1.7	3514	33	
(<i>t</i> Bu ₂ C=N)TiCl ₂ Ind	44 mg (118 mmol)	1.012	25	Homo	13.8	76405	767	68.24
(<i>t</i> Bu ₂ C=N)TiCl ₂ (C ₄ M ₈ F)	44 mg (110 mmol)	0.999	26	Co	22.4	89295	896	
			31	Homo	10.9	41404	419	79.47
			33	Co	11.4	36319	368	
			29	Homo	1	3134	30	84.15
			29	Co	0.6	2140	21	

¹ Support is Witco/MAO SiO₂ TA 02794/HL/04² Ethylene homopolymerization (Homo) or Ethylene-Butene copolymerization (Co)³ Pe = Polyethylene

INDUSTRIAL APPLICABILITY

This invention is suitable for olefin polymerization, particularly the solution polymerization of ethylene. The resulting ethylene polymers are suitable for a preparation of a wide variety of goods including, for example, molded goods and film.

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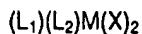
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CLAIMS

1. A catalyst system for olefin polymerization comprising:
 - a) a catalyst which is an organometallic complex of a group 4 metal; and
 - b) an activator,
 characterized in that such organometallic complex contains a ketimide ligand.

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2. The catalyst system according to claim 1 wherein said organometallic complex further contains a cyclic ligand which forms a delocalized pi-bond with said group 4 metal.
3. The catalyst system according to claim 1 wherein said organometallic complex is defined by the formula:



wherein M is a metal selected from Ti, Hf and Zr;

L₁ is a ketimide ligand;

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L₂ is a delocalized cyclic ligand which forms a pi-bond with said M and each X is a non-interfering ligand.

4. The catalyst system according to claim 3 wherein L₂ is a cyclopentadienyl-type ligand and each X is independently selected from halogen, hydrogen, hydrocarbyl having up to 10 carbon atoms, amido and phosphido.

5. The catalyst system according to claim 3 wherein said organometallic complex is defined by the formula:

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Cp Sub 1

\ /

M — N = C

/ \ \

X X Sub 2

wherein: said M is selected from Ti and Zr;
 said Cp is a cyclopentadienyl-type ligand;
 each of said X is a non-interfering ligand;

and each of said Sub 1 and Sub 2 is independently selected from hydrocarbyls having from 1 to 20 carbon atoms, silyl groups, amido groups and phosphido groups.

6. The catalyst system according to claim 5, wherein said M is titanium, said Cp is a cyclopentadienyl ligand, each of said Sub 1 and Sub 2 is a tertiary butyl group and each of said X is selected from halogen and methyl.

10 7. The catalyst system according to claim 1 wherein said activator is an alumoxane.

8. The catalyst system according to claim 7 in supported form, further characterized in that said alumoxane is methalumoxane.

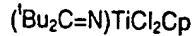
9. The catalyst system according to claim 1 in homogeneous form, further characterized in that said activator comprises a substantially non-coordinating anion.

10 20 10. The catalyst system according to claim 8 wherein a catalyst support selected from silica, alumina and silica-alumina is employed to synthesize said supported form.

11. A process for the copolymerization of ethylene and at least one additional alpha olefin having from 3 to 8 carbon atoms characterized in that said process employs the catalyst system according to claim 1.

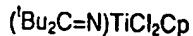
12. The process according to claim 11 when conducted in a gas phase, or slurry reactor, further characterized in that said catalyst system is in supported form.

13. The process according to claim 12 wherein said organometallic 30 complex is defined by the formula:



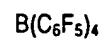
14. The process according to claim 11 when conducted in a medium pressure solution polymerization process.

15. The process according to claim 14 wherein said organometallic complex is defined by the formula:



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16. The process according to claim 15 wherein said activator comprises a substantially non coordinating anion defined by the formula:



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INTERNATIONAL SEARCH REPORT

Int. Search Application No
PCT/CA 98/00839

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C08F10/00 C08F4/64	
According to International Patent Classification (IPC) or to both national classification and IPC	
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C08F	
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched	
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)	
C. DOCUMENTS CONSIDERED TO BE RELEVANT	
Category *	Citation of document, with indication, where appropriate, of the relevant passages
A	<p>LATHAM ET AL: "The chemistry of dinitrogen residues. Part 1. Diazenido complexes of titanium, and some substituted analogs. X-ray crystal structures of dichloro(.eta.-cyclopentadienyl)(N₂-phenyl)diazenido- N₁,N₂)titanium(IV), -(butyl-tert-butylmethylenamido-N)titanium(IV), and -(triphenylphosphoranediylamido-N)ti" JOURNAL OF THE CHEMICAL SOCIETY, DALTON TRANSACTIONS, vol. 2, 1986, pages 377-386, XP002078049 see page 379, paragraph 3 - page 383; figure 4</p> <p style="text-align: center;">--- -/-</p>
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.	
<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"8" document member of the same patent family</p>	
Date of the actual completion of the international search	Date of mailing of the international search report
3 December 1998	17/12/1998
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl Fax: (+31-70) 340-3016	Authorized officer Gamb, V

Fcm PCT/ISA210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Int	national Application No
PCT/CA 98/00839	

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 739 905 A (IDEMITSU KOSAN CO) 30 October 1996 see preparation example 1 and examples 1, 2 -----	1-9,11
1		

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l. Search Report No.

PCT/CA 98/00839

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0739905	A 30-10-1996	JP	8134122 A	28-05-1996
		DE	69503355 D	13-08-1998
		DE	69503355 T	12-11-1998
		US	5807940 A	15-09-1998
		WO	9615160 A	23-05-1996